asymmetric induction upon incorporation of a chiral substituent at the olefinic centers (C$_1$, C$_5$, C$_6$). In the hope of assisting such a goal, we offer the following predictions: (1) Replacement of the C$_6$ allylic oxygen with other electron-rich atoms, e.g., N, S, P, and halogens, will give rise to a similar sense of selectivity. (2) Replacement of the C$_6$ allylic oxygen with an electropositive group, such as trimethylsilyl, will result in a reversed sense of diastereofacial control, i.e., approach of the "ester enolate" syn to silyl, from a hydrogen-eclipsed conformation. (3) C$_5$ substituent effects on *diastereofacial selectivity* will mirror those seen for analogous C$_6$ substitution. (4) Transposition of the allylic chirality at C$_5$ or C$_6$ to C$_1$ (both geometric isomers) will result in an opposite sense of diastereofacial selectivity, provided that there are similar conformational preferences about the two allylic centers.

Finally, we suggest that evaluation of ground-state conformer reactivity via molecular electrostatic potentials provides a powerful tool for assessing reaction energetics early along the reaction coordinate, where stereoselectivity in kinetically controlled asymmetric transformations may be addressed.[8-10,12] While unlikely to provide quantitative descriptions of resultant product distributions (as in rigorous transition-structure studies), reactivity models based on Coulombic potentials allow discussion of the means by which electronic asymmetry affects the reactivity of chiral substrates.

Acknowledgment. We gratefully acknowledge the discussions and insightful comments of Professors R. M. Coates (University of Illinois), D. P. Curran (University of Pittsburgh), and J. J. Gajewski (Indiana University). S. D. K. acknowledges a Fellowship from Churchill College during his tenure in Cambridge.

The Transient Species in Radical Chlorination in Benzene Solvent

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Received June 9, 1987

Although all data on selectivity in alkane chlorination in complexing solvents such as benzene are consistent with two chain carriers, a low selectivity intermediate (LSI) and high selectivity intermediate (HSI), there is controversy as to their nature. Data and arguments are reviewed concluding that there are no valid reasons for rejecting a Cl$^\bullet$–benzene π complex (πC) as the HSI. Data in which intermediates are trapped by maleic anhydride or excess Cl$_2$ are too fragmentary and contradictory to identify the HSI, although chemical intuition suggests that trapping could involve a small concentration of chlorocyclohexadienyl radicals (CCH) also present in the system. The best basis for identifying the HSI are the transient spectra reported by Ingold et al., and there is no convincing reason for rejecting their identification of it as πC.

The selectivities observed in free radical chlorinations are strikingly enhanced when they are carried out in benzene, other aromatic media, and a few other solvents, most notably CS$_2$.[1,2] The phenomenon is well-known, and Russell's original interpretation in terms of the formation of a Cl$^\bullet$–solvent π complex showing higher selectivity than uncomplexed Cl$^\bullet$[1] has been generally accepted, although for many years little more was published on the matter.

In 1983 interest was revived by a brief communication by Skell,[3] who reported that selectivities also depended on substrate concentration, increasing markedly as this was descreased. He proposed that, in addition to free Cl$^\bullet$ and its π complex, a σ complex, i.e., in the case of benzene the chlorocyclohexadienyl radical, was involved in the reaction. The incipient controversy gained momentum in 1985 when Ingold and co-workers[4] confirmed Skell's selectivity data for 2,3-dimethylbutane (DMB) in benzene but showed that all data were consistent with a kinetic scheme involving only two species of distinguishable selectivity. They further investigated the transients involved in the reaction by a series of elegant experiments involving fast laser spectroscopy, assigned rate constants to the steps in their scheme, and, from observed spectra and the insensitivity of their observed kinetics to O$_2$, concluded that the high selectivity intermediate (HSI) was indeed Russell's π complex, while the low selectivity intermediate (LSI) is uncomplexed Cl$^\bullet$. Skell[5] has now published his data in detail and accepts the form and rate constants of Ingold's analysis but identifies the HSI as the chlorocyclohexadienyl radical (CCH) with the LSI being free Cl$^\bullet$ and its π complex (πC), considered to have similar selectivities. His most significant argument (of several) involves data on the competition between alkane chlorination and two other long-known reactions of the Cl$_2$–benzene system: the formation of hexachlorocyclohexane at high Cl$_2$ concentrations, and the induced conversion of maleic anhydride to 2-chloro-3-phenylsuccinic anhydride.[6] Although neither reaction has had definitive study, both have long been considered to involve the chlorocyclohexadienyl radical as a plausible intermediate[7] and accordingly in Skell's scheme should act as traps for the HSI.

In this paper I review these trapping experiments and some of Skell's other arguments to see if there are, in fact, valid criteria other than Ingold's fast spectroscopic data for identifying the HSI. My conclusion is that there are not. The trapping data yield only fragmentary and inconsistent results when analyzed in terms of the model,

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(1) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 2977; **1958**, *80*, 4987, 4997.

(2) Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 1485.

(3) Skell, P. S.; Baxter, H. N., III; Taylor, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 120.

(4) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.

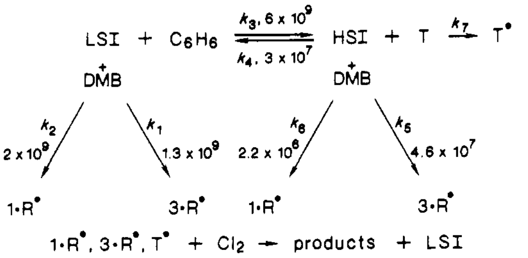
(5) Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300.

(6) Ecke, G. G.; Buzbee, L. R.; Kolka, A. J. *J. Am. Chem. Soc.* **1956**, *78*, 79.

(7) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 308–310.

and other arguments are inconclusive. I suggest that the spectroscopic and product data together are best accommodated by a scheme in which the HSI is πC, which either reacts directly with the traps or is in turn in quasi-equilibrium with a small amount of CCH. This CCH does not react with alkanes but goes on to react with Cl_2 and maleic anhydride by what are evidently complex processes.

Trapping Experiments and the LSI–HSI Hypothesis. The reaction scheme of Ingold and Skell, extended for DMB in benzene to systems including a trap (T) is shown in eq 1.[8] The scheme in eq 1 assumes that Cl• is



(1)

"born" as the LSI and that traps only react with the HSI. From eq 1 the steady-state expression for the HSI is given in eq 2, and the observed selectivity, S, is given by eq 3,

$$k_3[\mathrm{LSI}][\mathrm{C_6H_6}] = \{k_4 + (k_5 + k_6)[\mathrm{DMB}] + k_7[\mathrm{T}]\}[\mathrm{HSI}] \tag{2}$$

$$S = S_\mathrm{L}\{(k_4/k_6) + (1 + S_\mathrm{H})[\mathrm{DMB}] + (k_7/k_6)[\mathrm{T}]\} + S_\mathrm{H}(k_3/k_2)[\mathrm{C_6H_6}]/(k_4/k_6) + (1 + S_\mathrm{H})[\mathrm{DMB}] + (k_7/k_6)[\mathrm{T}] + (k_3/k_2)[\mathrm{C_6H_6}] \tag{3}$$

where $S_\mathrm{L} = k_1/k_2$ and $S_\mathrm{H} = k_5/k_6$, the selectivities of the LSI and HSI, respectively. S_L can be measured independently in the absence of benzene, and multiple regression analysis by Ingold and Skell of numerous data in the absence of traps yielded the other ratios S_H, k_4/k_6, and k_3/k_2. The two sets of data are in substantial agreement, and the fit between calculated and observed S's impressive, e.g., for Skell's data the median difference is 5% of S, close to the experimental uncertainties of the measurements. In addition to these ratios, Ingold has directly measured three quantities, $k_1 + k_2$, k_3, and k_5. From these he calculated the values given in eq 1. Using the above ratios, we can approach the much scantier data on trapping experiments. From eq 3, four experiments in the presence of maleic anhydride give $k_7/k_6 = 130$, 86, 57, and 122, average 99, whence k_7 for MA = 2.2×10^8 (Skell gives 2×10^8). Two experiments at high Cl_2 give $k_7/k_6 = 13$ and 15, whence k_7 for $Cl_2 = 3.1 \times 10^7$ (Skell gives 3×10^7).[9]

There is another and I believe more direct way of determining k_7 in trapping experiments and this is by considering relative yields. From eq 1 one can also derive the relation in eq 4, where R is the ratio of fractional yield of

$$R = \frac{\Delta[\mathrm{DMB}]/[\mathrm{DMB}]}{\Delta[\mathrm{T}]/[\mathrm{T}]} = \frac{k_4/k_7 + [\mathrm{T}] + (k_5 + k_6)[\mathrm{DMB}]/k_7}{k_3[\mathrm{C_6H_6}]/(k_1 + k_2)} + \frac{k_5 + k_6}{k_7} \tag{4}$$

DMB and T derived products. Since all other quantities are known, k_7 can easily be calculated. Yields of DMB products are available for three experiments in the presence of maleic anhydride. MA derived products are not given, but plausible maximum values can be calculated by assuming that they equal the decreases in yield of alkyl chlorides from those observed without MA. Calculation gives k_7 for MA 1.4, 1.0, and 1.5 all $\times 10^7$, average 1.3×10^7.[10] None of the Cl_2-trapping experiments with DMB give suitable yield data to calculate k_7, but, assuming that neopentane shows the same reactivity as the primary hydrogens of DMB, a calculation can be made from at least one experiment with this substrate[11] and gives k_7 for $Cl_2 = 9 \times 10^5$. The discrepancies between the use of eq 3 and 4 to calculate k_7's are very large (factors of 17 and 34 for MA and Cl_2, respectively) particularly when compared with the excellent consistency of the data in the absence of traps. To me, this indicates that something is seriously lacking in the model.[12,13] Thus using k_7 from selectivity data predicts a RCl yield of under 4% in a MA experiment where the actual yield was 43%.

If I had to choose between the two, I would prefer the values derived from relative yields as involving a simpler and more direct measurement, and it is unfortunate that yields were not investigated in more detail. Thus, in eq 4 at high benzene concentrations $R \simeq (k_5 + k_6)/k_7$, and the first term on the right-hand side of the equation is just a small correction due to a little reaction going through the LSI. On the other hand, selectivities are much more sensitive to this correction and assume that a complex kinetic scheme is being exactly followed.

As matters stand, I question whether these trapping experiments show more than that alkane chlorination and reactions with Cl_2 and maleic anhydride compete, as would be required by any scheme involving Cl• chains, give some idea of relative rates and indicate that the trapping reactions are complex. In the case of Cl_2, this is also evident from Ingold's work, since high levels of Cl_2 increased the rate of disappearance of the HSI with an apparent second-order rate constant of 2×10^6. Since the reaction of the HSI with Cl_2 to give dichlorocyclohexadiene and Cl• would have been kinetically invisible under their conditions, the nature of the reaction is unknown, although the rate constant is close to my calculated value of k_7.

The even more complex case of MA trapping cannot be pursued further without adequate analysis of the products actually formed. However, if the reaction of the HSI (or whatever species is involved in the trapping) with MA is fast enough to compete with reaction with Cl_2, the same might be expected for reaction with the alkyl radicals derived from DMB, and, if so, alkylchlorosuccinic anhydrides should be found among the products. This would imply a large polar effect facilitating such additions[14] and could lead to the selective removal of tertiary alkyl radicals, thus changing the apparent selectivity of DMB chlorination in the direction Skell reports.[15]

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[8] I have used Ingold's numbering system for k's but Skell's LSI–HSI terminology for the two transients, since the kinetics are independent of what they actually are. I also use molar selectivities S (equivalent to Ingold's S^{m}'s) rather than selectivities per H (r's). For DMB $r = 6S$. Some duplication of previous derivations[4,5] is necessary to clarify my discussion.

[9] Data from Tables X and VIII of ref 5, respectively.

[10] These estimated yields and k_7's are almost certainly high since the MA reaction gives considerable polychlorinated material and other products.[6]

[11] Data from the third entry of Table IX of ref 5, using average concentrations of RH and Cl_2. The other entries show too large changes in concentrations for reliable calculation.

[12] These same discrepancies also arise in the ratios $(k_5 + k_6)/k_7$, obtained directly from eq 4 and the other ratios derived from the selectivities observed in the absence of traps, so they are not the consequence of any uncertainties in absolute rate measurements.

[13] Skell has also noted these discrepancies in a footnote but considers them smaller than I calculate and prefers to treat them as unimportant.

[14] The extraordinarily high reactivity of maleic anhydride toward electron-rich radicals was first detected in copolymerization (cf. Chapter 4 of ref 7) and is well-known. E.g., toward cyclohexyl radicals, MA is 730 times as reactive as styrene: Giese, B.; Maxner, J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 154.

Diffusion and π Complexes. The rate constants for reaction of the LSI with DMB and benzene, $k_1 + k_2$ and k_3, were measured at very low concentrations of substrates, and the rate constants 3.3×10^9 and 6×10^9 indicate that the reactions are close to diffusion controlled. On the other hand, the selectivity data used in the analysis of eq 3 chiefly involved systems in which the concentrations of one or both substrates were 1 M or greater. This dichotomy has been used by Skell in some of his arguments, so I shall consider its significance. The observed rate constant of a bimolecular reaction may be considered as a diffusion constant multiplied by the probability that the collision complex reacts, rather crudely, $k_{\text{obsd}} = k_d k/(k + k_d)$, where k is the "intrinsic" rate constant for reactions. With diffusion controlled rates $k > k_d$. If the concentration of one reactant increases, we reach the point (approximately 1 M if we assume that each molecule has an average of 10 "near neighbors", a little less than close packing) where the other lower concentration reactant is usually in a collision complex with one or more of the high concentration species and the need for translational diffusion defined by k_d disappears. Our k_{obsd} should now become k (which may still involve a rotational diffusion or other reorientation term), and, for a reaction near diffusion control at low concentrations, k_{obsd} would be expected to increase. Similarly, observed ratios of rate constants (at least one of which is diffusion controlled) could change with concentration, although, as a first approximation, equilibrium constants involving a diffusion controlled step should not.[16]

The fitting of eq 3 involves determining three ratios of rate constants: k_5/k_6, k_4/k_6, and k_3/k_2. Of these, k_3 and k_2 are potentially diffusion controlled and might show a concentration dependence.[17] However, this is not observed. Ingold's and Skell's "best fits" for k_3/k_2 are in substantial agreement with the ratio calculated from Ingold's kinetic measurements at high dilution.[18] The conclusion seems to be that k_2 and k_3, if they could be measured at high substrate concentrations, would not be much larger than the values that Ingold reports.[18]

Skell has made use of two arguments connected with diffusion control in his efforts to identify CCH as the HSI and still place πC in his reaction scheme. The first is that formation of πC should be faster at high benzene concentrations than k_3 indicates, since the formation of the benzene–I$^{\bullet}$ complex in neat benzene is complete in a few picoseconds.[19] Actually, $k_3 = 6 \times 10^9$ predicts a half-life for Cl$^{\bullet}$ of 1×10^{-11} s in benzene, so any difference is trivial.

The second argument is more complex. Both Skell[20] and Ingold[4] have noted that at low concentrations in CCl_4 or similar inert solvents, dilute DMB gives substantial yields of polychlorinated products even at low conversions but not in the presence of substantial amounts of benzene. Skell has explained this on the basis that the reaction in eq 5 leaves RCl and Cl$^{\bullet}$ in the same solvent cage, so, if H

$$R^{\bullet} + Cl_2 \rightarrow RCl + Cl^{\bullet} \qquad (5)$$

abstraction from RCl is sufficiently fast, it will compete with Cl$^{\bullet}$ escape into the solution, a conclusion quite in keeping with Ingold's rate constants. Skell's argument now is that, if Cl$^{\bullet}$ is not immediately converted into πCl (assumed less reactive, but still a LSI) polychlorination should still be observed in benzene which he states not to be the case. I believe the data do not support this. From Skell's data,[20] in inert solvents DMB initially gives a 1.7:1 ratio of mono and dichlorides; i.e., cage escape is almost twice as fast as reaction. If cage escape, HSI formation and reaction are treated as competing reactions, RCl is considered to have the same reactivity as DMB, and the "effective concentration" of RCl in the cage is taken as 1 M (i.e., one of about 10 near neighbors), the fraction dichloride should be $1/(1 + 1.7 + 1.82[C_6H_6])$, i.e., 22% and 16% in 1 and 2 M benzene, respectively. Actually RCl is almost certainly *less* reactive than DMB, and if it were half as reactive, the calculated yields would be 16 and 10%. These numbers may be compared with Ingold's data for 0.1 M DMB: >15% dichloride in 1 M benzene, but <15% in 2 M.[21] Any assumption about "fast πC formation" seems unnecessary.[22]

Transient Spectra. If no other data or arguments unequivocally identify the LSI and HSI species, we are left with Ingold's transient spectra. Spectra of several cyclohexadienyl radicals are known. All show strong absorption of 300–320 nm and, at most, very weak absorption in the visible.[23] Species identified as Br$^{\bullet}$– and I$^{\bullet}$–benzene π complexes (and also many similar π complexes) show broad absorption at 400–600 nm. In general, their short wavelength spectra have not been reported. The HSI spectrum shows a broad peak at 400–600 nm but also absorption at 300–320 nm, significantly different from that of the unsubstituted cyclohexadienyl radical. These two peaks appear and disappear together, and their relative intensities remain constant over a wide temperature range. On this basis Ingold considers them as arising from a single species and assigns it the πC structure, as Buhler had done previously with the very similar spectra which he had observed on high energy irradiation of CCl_4 in benzene,[24] although he recognizes that a small amount of CCH may contribute to the short-wavelength region. This assignment seems eminently plausible to me.

At present these spectra provide the best identification of the HSI, and I find it hard to give weight to arguments against Ingold's and Buhler's assignment.

Finally, it should be emphasized that even if Skell's trapping experiments had been consistent simultaneously with eq 3 and 4, they would not have distinguished be-

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[15] In contrast, Aver'yanov and Ruban (Aver'yanov, V. A.; Ruban, S. G. *Kinet. Katal.* **1986**, *27*, 485) report that in chlorobenzene and dichlorobenzene selectivity in chlorination of 1,1-dichloroethane shows *no* sensitivity to high Cl_2 concentrations despite significant Cl_2 addition to solvent and use this as an argument against any CCH as the HSI.

[16] This follows from thermodynamics, providing there are not peculiar intermolecular interactions in the collision complex. More specifically, for diffusion controlled formation of a complex if $k_f(\text{obsd}) = k_d k_f/k_d + k_f)$ then $k_b(\text{obsd}) = k_b k_d/(k_d + k_f)$, $k_f(\text{obsd})/k_b(\text{obsd}) = k_f/k_b$. The complex relaxes to a collision complex which then has to separate to complete dissociation, so diffusion slows reaction in both directions.

[17] Also, since k_4 comes from measurements at high benzene concentrations, the HSI $\rightleftarrows$ LSI equilibrium constant would be too small, although this has no effect on the curve fitting.

[18] The largest discrepancy would be expected for systems with DMB < 1 M, benzene < 1 M, where k_3 should have increased but k_2 should not have. There is no clear difference in the fit of these points and the others.

[19] Hilinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1985**, *107*, 5907.

[20] Skell, P. S.; Baxter, H. N., III. *J. Am. Chem. Soc.* **1985**, *107*, 2823.

[21] These data have been confirmed by a more detailed study. Dichloride yields decrease smoothly but do not vanish as benzene concentrations are increased: Ingold, K. U., private communication.

[22] Two other arguments for πC not being the HSI seem even more conjectural. One is that the k_3/k_4 is too large for the πC/Cl$^{\bullet}$ equilibrium, since the π complex equilibria for I$^{\bullet}$, I_2, and Cl_2 are all near unity. On the other hand, the electron affinity of Cl$^{\bullet}$ is 13 kcal greater than that for I$^{\bullet}$. Second, since Cl_2 exists largely as its π complex at high benzene concentrations, Cl$^{\bullet}$, formed in reaction 5 should be "born" as πC. On the other hand, reaction 5 is exothermic by some 23 kcal. This might well give Cl$^{\bullet}$ enough kinetic energy to break any such weak bonding. I find neither argument convincing.

[23] Consideration of their ESR spectra[5] seems irrelevent, since such spectra have not been reported in these systems.

[24] Buhler, R. E. *Helv. Chim. Acta* **1968**, *51*, 1558. Buhler's and Ingold's experimental conditions and their observed kinetics of transient disappearance are, however, both quite different.

tween a fast and somewhat unfavorable equilibrium (eq 6) followed by reaction of the CCH with the trap, or direct

$$\pi C \overset{k_6}{\rightleftharpoons} CCH \tag{6}$$

reaction of πC with the trap. Skell has argued against the former on the basis that equilibration involving covalent bond formation (eq 6) should be slower than equilibration forming a π complex. This argument is unconvincing, since bond-forming reactions of $Cl^\bullet$ are often diffusion controlled (as here) and the only requirement here is that the equilibration in eq 6 be slower than the relatively slow dissociation of πC (k_4), i.e., that CCH be less stable than πC but more stable than the LSI. A more valid criticism is that if K_6 is small, rate constants for reaction of CCH with traps would have to be even faster than the k_7's calculated above. From his spectra Ingold estimated $K_6 < 0.1$ and, from the lack of effect of O_2 on the disappearance of the HSI, $K_6 < 0.01$. This latter estimate is complicated by the fact that Skell did observe competition between reactions of the chain carrier with O_2 and Cl_2 and could be too low.

Skell has objected to direct reaction of πC with maleic anhydride as being unprecedented and involving concerted formation of two σ bonds and the opening of a π bond. The same objection could be raised to his postulated reaction of CCH with DMB, which forms a σ and a π bond and breaks two σ bonds. It may be that this is another case where two models, πC and CCH, lie at the extremes of what is actually a continuum. The structures of only a few π complexes are known, and "πC" could be anything from a centrosymmetric species, to one which is quite asymmetric with the Cl approaching bonding to a single carbon although still showing a "charge-transfer-type" spectrum. What species it is that actually reacts with Cl_2 and MA, in short, remains unknown.

Optical Resolution of Phosphinates and Phosphine Oxides by Complex Formation with Optically Active 2,2'-Dihydroxy-1,1'-binaphthyl and Crystallographic Study of Two Diastereomeric Complexes with $(CH_3)(C_6H_5)(OCH_3)PO$

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Received August 7, 1987

Some [(alkyl-substituted)arene]phosphinates and -phosphine oxides have been resolved efficiently by crystalline complexation with optically active 2,2'-dihydroxy-1,1'-binaphthyl (**1**). Two diastereomeric 1:1 complexes of the latter with a representative phosphoric ester $(CH_3)(C_6H_5)(CH_3O)P{=}O$ (**2a**) were studied by X-ray diffraction methods in order to characterize the geometric pattern of intermolecular interaction. They form very similar crystal structures in space group $P2_1$ which consist of continuous chains of hydrogen-bonded species. Along the chains, **2a** is located between and bound (through its PO nucleophile) simultaneously to two adjacent molecules of **1**, while **1** donates its OH protons to two different molecules of **2a**. Steric forces that involve the lipophilic substituents and steric barriers on the interacting components play an important role in determining the crystal packing arrangements and effecting mutual recognition.

Introduction

Only a few preparative methods of optically active phosphinates and phosphine oxides have been reported so far. Menthane phosphinates derived from (−)-menthol were resolved by repeating recrystallization several times from hexane,[1] and the optically active species so obtained were converted into the corresponding optically active phosphine oxides by a stereoselective reaction with Grignard reagents.[1,2] Optically active phosphorous compounds derived from carbohydrates,[3] (−)-ephedrin,[4,5] and (−)-prolinol[6] have also been prepared by resolution, and their conversion into optically active phosphorus compounds by selective reactions with organometallic reagents is known. These methods, however, require natural products as a chiral source (menthol, carbohydrates, ephedrin, proline), and the selectivity of the conversion of diastereomeric phosphorus compounds derived from the natural product to phosphine oxides, phosphinates, and phosphonates is always limited to some extent.[1-6]

On the other hand, it has recently been reported that sulfoxides[7,8] and selenoxides[9] are easily resolved by complexation with optically active 2,2'-dihydroxy-1,1'-binaphthyl (**1**). This method is very simple and does not require natural products. It gives 100% optically pure compound since the resolution can easily be repeated, or the complex with **1** can be purified by recrystallization. Moreover, the enantiomeric derivatives of the compound can be resolved separately by complexation with the cor-

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(1) Korpium, O.; Lewis, R. A.; Chickos, J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4842.

(2) Lewis, R. A.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7009.

(3) Cooper, D. B.; Inch, T. D.; Lewis, G. J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1043.

(4) Cooper, D. B.; Hall, C. R.; Harrison, J. M.; Inch, T. D. *J. Chem. Soc.* **1977**, 1969.

(5) Hall, C. R.; Inch, T. D.; Lawson, I. W. *Tetrahedron Lett.* **1979**, 2729.

(6) Koizumi, T.; Yanada, R.; Takagi, H.; Hirai, H.; Yoshii, E. *Tetrahedron Lett.* **1981**, *22*, 477 and 571.

(7) Toda, F.; Tanaka, K.; Nagamatsu, S. *Tetrahedron Lett.* **1984**, *25*, 4929.

(8) Toda, F.; Tanaka, K.; Mak, T. C. W. *Chem. Lett.* **1984**, 2085.

(9) Toda, F.; Mori, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1357.

0022-3263/88/1953-0308$01.50/0